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**Title: Fire Extinguishing Composition**

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**For: DuPont Corporate Information Science**

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(54) Title of the Invention: **Fire Extinguishing Composition**

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### SPECIFICATION

#### 1. Title of the Invention

Fire Extinguishing Composition

## 2. Claims

1. A fire extinguishing composition comprising a mixture of one or more types of substance selected from the group consisting of proteins, protein decomposition products and surfactants; an aqueous solution containing one or more types of liquid polyhydroxy compound and one or more types of polyhydroxy compound; and one or more types of halogenated hydrocarbon.

2. A fire extinguishing composition produced by mixing or dispersing in water a mixture of one or more types of substance selected from the group consisting of proteins, protein decomposition products and surfactants; an aqueous solution containing one or more types of liquid polyhydroxy compound and one or more types of polyhydroxy compound; and one or more types of halogenated hydrocarbon.

## 3. Detailed Description of the Invention

The present invention relates to a fire extinguishing composition whereby the performance of halogenated hydrocarbon-based fire extinguishing agents that are used in extinguishing fires is improved. Specifically, the invention relates to a halogenated hydrocarbon-based fire extinguishing composition with improved fire extinguishing capacity and fire extinguishing persistence. In addition, the present invention relates to a fire extinguishing composition that readily emulsifies or disperses when mixed with water and delivers excellent fire extinguishing performance.

In recent years, halogenated hydrocarbon-based fire extinguishing agents with negative catalytic action have appeared on the market, and their utilization in fire extinguishing equipment has been increasing. This increase is due to characteristics whereby increased fire extinguishing power is produced for a given amount of fire extinguishing agent, a broader fire extinguishing area is ensured, and secondary staining is prevented from being caused by the fire extinguishing agent.

However, halogenated hydrocarbon-based fire extinguishing agents extinguish fires by discharging fire extinguishing gas into the air surrounding the fire being extinguished.

Consequently, although their fire extinguishing effects are adequate for enclosed indoor areas and for localized fires in large enclosed areas, the fire extinguishing gas disperses and flows over a broad area when extinguishing fires in outdoor areas or rooms that have open windows or doors (openings), thus creating problems. In addition, the extinguishing targets for light water compositions are primarily limited to oil surface fires. These fire extinguishing agents cannot be used in fires within structures such as buildings, and thus their capacity for general use is low.

In addition, foam fire extinguishing agents based on protein foam or surfactants should preferably generate foam that remains adhered to the surface of the combusting material for a long time or, in other words, the foam should be retained for a long time after the foam film has been formed. A material is also preferred that does not require a foamer or other device in the fire extinguishing liquid discharge section at the tip of the foam fire extinguishing line, as is required with existing foam fire extinguishing equipment.

The inventors of the present invention et al. carried out various investigations with the objective of developing a fire extinguishing agent having second-order fire extinguishing capacity while also achieving improvements in the above areas. As a result, the present invention was perfected upon discovering that when the aforementioned halogenated hydrocarbons are mixed as needed with special materials along with water, a fire extinguishing composition is obtained that is readily emulsified and dispersed in water and has the following characteristics:

- 1) maintenance of fire extinguishing capacity over long periods of time,
- 2) secondary fire extinguishing capacities and
- 3) foamability without requiring a foamer.

Specifically, the fire extinguishing composition of the present invention is a composition comprising a mixture of one or more types of substance selected from the group consisting of proteins, protein decomposition products and surfactants; an aqueous solution containing one or more types of liquid polyhydroxy compound and one or more types of polyhydroxy compound; and one or more types of halogenated hydrocarbon, and is also a composition produced by emulsifying or dispersing this mixture in water.

It is preferable for the aforementioned mixture to be a uniform liquid, paste or solid mixture that is produced by emulsifying, microemulsifying or solubilizing the halogenated hydrocarbon in a liquid polyhydroxy compound or polyhydroxy compound aqueous solution.

Examples of water-soluble proteins used in the present invention include casein sodium, soy protein, defatted powdered milk, whey flour, raw egg white, dried egg white, blood powder, meat powder, microbial protein, peptone, yeast extract, albumin, lactoalbumin, globulin, lactoglobulin, glutelin, protamin and histamine. In addition, examples of protein decomposition products that may be used are compounds produced by the decomposition of the above types of protein using protease, acid and other substances.

In addition, examples of surfactants that may be used are various anionic, nonionic, cationic and amphoteric surfactants. Examples of anionic surfactants that may be cited include soap, N-acyl amino acid salts, alkyl ether carboxylic acids, acylated peptides and other carboxylic acid salts; alkylsulfonic acid, alkylbenzene, sulfonates, alkyl naphthalene sulfonates and formalin condensates thereof, dialkylsulfosuccinate esters,  $\alpha$ -olefin sulfonic acids, N-acylmethyltaurine and other sulfonates; sulfated oils, alkyl sulfates, alkyl ether sulfates, alkyl amine [sic; possibly "amine"] ether sulfates, alkyl amide sulfates and other sulfate ester salts; and alkyl phosphates, alkyl ether phosphates, alkyl allyl ether phosphates and other phosphate ester salts. In addition, examples of nonionic surfactants that may be cited include polyoxyethylene alkyl ethers, polyoxyethylene secondary alcohol ethers, polyoxyethylene alkyl phenyl ethers, alkylphenol formalin condensates and other ethylene oxide derivatives; polyoxyethylene-polyoxypropylene block polymers and other ether-based surfactants; polyoxyethylene glycerin fatty acid esters, polyoxyethylene castor oil or hardened castor oil, polyoxyethylene sorbitan fatty acid esters, polyoxyethylene sorbitol fatty acid esters and other ether ester type surfactants; polyoxyethylene glycol fatty acid esters, fatty acid monoglycerides, sorbitan fatty acid esters, sucrose fatty acid esters and other ester-based active agents; and fatty acid alkanolamides, polyoxyethylene fatty acid amides, polyoxyethylene alkylamines, alkylamine oxides and other nitrogen-containing active agents. In addition, examples of cationic surfactants that may be cited include alkylamine salts, quaternary ammonium salts, benzalkonium salts, benbitonium [sic; possibly "benzethonium" - translator] chloride and pyridinium salts. Examples of amphoteric surfactants that may be cited include carboxybetaine, sulfobetaine, aminocarboxylate,

imidazolinium betaine and lecithin. Alternatively, fluorine-based surfactants and silicone-based surfactants may also be used. The fire extinguishing composition of the present invention employs one or more types of substance selected from the group consisting of proteins, protein decomposition products and surfactants as essential components, but among these substances, it is particularly desirable to use proteins and protein decomposition products.

In addition, examples of polyhydroxy compounds that may be used include propylene glycol and other dihydroxy alcohols; glycerin and other trihydroxy alcohols; sorbitol mannitol and other sugar alcohols; glucose, lactose and other simple sugars; sucrose, maltose, galactose and other disaccharides; trisaccharides and higher order sugars; and various invert sugars obtained by starch hydrolysis, as well as starch syrup, dextrin isomerized sugar, syrup, honey, jams and other such substances. Examples of liquid polyhydroxy compounds that may be used include substances selected from polyhydroxy compounds that are liquids at normal temperatures, such as propylene glycol and glycerine.

Concerning the ratios of use of the various components of the present invention, the amount of one or more types of substance selected from the group consisting of proteins, protein decomposition products and surfactants is 0.005% or greater (weight standard, likewise below), with 0.05% or greater being preferred, and 5% or greater being particularly desirable, with respect to the total amount of the aforementioned substances and the polyhydroxy compound or aqueous solution thereof. The polyhydroxy compound is preferably used in the amount of 30% or greater with respect to the total amount described above, with 40% or greater being preferred. This amount may be as much as nearly 100% when, for example, a liquid polyhydroxy compound is used.

The halogenated hydrocarbon used in the present invention is a compound wherein at least one hydrogen atom is substituted with a fluorine atom, chlorine atom, bromine atom or other halogen atom, examples of which include carbon tetrachloride, chlorobromomethane, chlorodifluoromethane, bromochlorodifluoromethane, bromotrifluoromethane, chlorodifluoromethane, trichlorofluoromethane, bromotrichloromethane, dibromodichloromethane, tribromochloromethane, bromodichlorofluoromethane, dibromochlorofluoromethane, tribromofluoromethane, dibromodifluoromethane, bromodichloromethane, dibromochloromethane, tribromo-

methane, bromochlorofluoromethane, dibromofluoromethane, bromodichloromethane, dibromomethane, dibromomethane, bromofluoromethane, bromomethane and other halogenated methanes; hexachloroethane, hexafluoroethane, dibromotetrafluoroethane, tetrachlorodifluoroethane, trichlorotrifluoroethane, dichlorotetrafluoroethane, chloropentafluoroethane, pentachloroethane, tetrachlorofluoroethane, trichlorodifluoroethane, dichlorotrifluoroethane, chlorotetrafluoroethane, pentafluoroethane, tetrachloroethane, trichlorofluoroethane, dichlorodifluoroethane, chlorotrifluoroethane, tetrafluoroethane, trichloroethane, dichlorofluoroethane, chlorodifluoroethane, trifluoroethane, dichloroethane, chlorofluoroethane, difluoroethane, fluoroethane and other halogenated ethanes; tetrachloroethylene, trichlorofluoroethylene, dichlorodifluoroethylene, chlorotrifluoroethylene, tetrafluoroethylene, trichloroethylene, dichlorofluoroethylene, chlorodifluoroethylene, trifluoroethylene, dichloroethylene, chlorofluoroethylene, difluoroethylene and other halogenated ethylenes; octafluoropropane, hexafluoropropylene and other halogenated propanes or halogenated propylenes; and hexafluorocyclopropane, tetrachlorotetrafluorocyclobutane, dichlorohexafluorocyclobutane and other halogenated cyclic hydrocarbons. In particular, halogenated hydrocarbons with carbon numbers of 1 to 4 and boiling points of  $-50$  to  $150^{\circ}\text{C}$  are preferred.

In addition to the above types of components, the fire extinguishing composition of the present invention can also contain various components such as bicarbonate, phosphate and other inorganic fire extinguishing agents; organic phosphorus compounds and other organic fire extinguishing agents; sodium alginate, carboxymethylcellulose, polyoxyethylene oxide and other thickeners; and colorants, fragrances, preservatives, antiseptic agents, antirust agents and other organic and inorganic substances.

It is preferable to manufacture the fire extinguishing composition of the present invention by mixing one or more types of substance selected from the group consisting of proteins, protein decomposition products and surfactants, an aqueous solution containing one or more types of liquid polyhydroxy compound and one or more types of polyhydroxy compound and a halogenated hydrocarbon, or alternatively, by the additional emulsification or dispersion thereof in water; or by mixing one or more types of substance selected from the group consisting of proteins, protein decomposition products and surfactants, and an aqueous solution containing one or more types of liquid polyhydroxy compound or one or more types of polyhydroxy compound

at normal temperature or under heating to prepare a mixture, by gradually adding and mixing the halogenated hydrocarbon therein under stirring to produce a composition, or alternatively, by subsequently dispersing or emulsifying the mixture in water. The halogenated hydrocarbon can be mixed as necessary under a reduced temperature or elevated pressure.

When the fire extinguishing composition of the present invention is a liquid, it may be used without being subjected to further treatments, but ordinarily it is preferable to disperse or emulsify the composition in water before using it as a fire extinguishing liquid. When preparing a fire extinguishing liquid from the fire extinguishing composition of the present invention, it is desirable to dilute the fire extinguishing composition of the present invention in water so that the halogenated hydrocarbon contained in the fire extinguishing liquid has a concentration of 10 to 50%.

The fire extinguishing composition of the present invention readily dissolves or disperses in water, and can therefore be mixed with water when necessary to prepare a fire extinguishing liquid that is then used on various types of fires. In addition, the fire extinguishing liquid can be foamed without using foaming equipment in order to have its foam fire extinguishing effects. In addition, the gas generated in the foam is halogenated hydrocarbon, not air. Moreover, the foam has a long persistence period, and thus superior fire extinguishing effects can be obtained even when using dramatically reduced amounts of halogenated hydrocarbon relative to when only halogenated hydrocarbons are used. Moreover, the superior fire extinguishing persistence extends over a long period of time, and the composition thus has reignition prevention effects (secondary fire extinguishing effects) whereby ignition will not occur if flame is applied after extinguishing. Consequently, the fire extinguishing composition has superior performance as a fire extinguishing composition.

Based on these considerations, the fire extinguishing composition of the present invention can be used for various types of fires as shown in Table 1 below, and in particular, the composition has significant advantages in that it can be used for localized-discharge fire extinguishing in open areas (non-sealed spaces) which have posed significant problems for fire extinguishing methods involving conventional halon gas discharge.



Table 1

Fire type			Use
Buildings/ structures	Medium or large	Underground structures and underground parking in buildings	Sprinkler equipment
	Small	Stores	Portable fire extinguishers
Household			Hand-held fire extinguishers
Factories	Dangerous materials/chemical plants Oil tanks		Foam fire extinguishers Fire extinguishing foam
	Other manufacture plants		Portable fire extinguishers
Tunnels			Sprinkler equipment
Automobiles	Engine compartment installations		Engine compartment fire extinguishing systems
	Driver seat standard equipment		Hand-held fire extinguisher

The present invention is described in additional detail below using working examples.

### Working Example 1

28.5 parts (weight standard, likewise below) of glycerine was heated to between 70 and 80°C, and 1.5 parts of casein sodium was gradually added under stirring. The casein sodium was dissolved or dispersed uniformly in the glycerine. After cooling, 70 parts of halon 2402 (dibromotetrafluoroethane) was added dropwise while stirring, and a fire extinguishing composition was thus obtained that consisted of a uniform mixture.

The fire extinguishing composition readily emulsified or dispersed when mixed with water, thus producing a fire extinguishing liquid composition. Subsequently, fire extinguishing liquids were prepared having the various concentrations presented in Table 2 below, and a fire extinguishing test was carried out by the following method. The results are presented in Table 2.

### Fire extinguishing test method

Gasoline was introduced at a depth of 15 mm into a pan with a diameter of 260 mm and a depth of 70 mm, and after ignition, a hand-pumped sprayer (1 stroke: 12.5 cc) containing fire extinguishing liquid was used in order to spray the composition at a constant rate. The fire extinguishing time and the volume of fire extinguishing liquid required for fire extinguishing were determined.

Table 2

Halon concentration in fire extinguishing liquid (%)	Fire extinguishing time (sec)	Amount of fire extinguishing liquid (cc)	Used amount of halon (cc)
2	Not extinguished	250	5
4	Same	250	10
5	Same	250	12.5
8	Same	250	20
10	9	225	22.5
15	5	225	34
20	15	200	40
30	15	175	52.5
50	5	87.5	44
Water	Not extinguished	250	0
Halon stock solution	5	40	40

The fire could not be extinguished with water alone, and about 40 cc was required for extinguishing when halon stock solution was used. However, halon is highly volatile, and reignition readily occurred when fire was applied immediately after extinguishing, and thus the halon stock solution was inappropriate for use in localized-discharge fire extinguishing methods. In contrast, the fire extinguishing liquid prepared using the fire extinguishing composition of the present invention was able to extinguish the fire with about half (22.5 cc) of the halon amount relative to when halon stock solution was used. The reason for this is not due simply to the cooling effect of the water in conjunction with the fire extinguishing effects of the halon, but due also to the fact that foaming of the fire extinguishing liquid prepared from the respective fire extinguishing compositions of the present invention occurs without the use of any foaming equipment. Consequently, in addition to the foam fire extinguishing effects, the gas in the foam is halon, not air, which produces superior fire extinguishing effects. Also, due to the aforementioned superior foam persistence of the fire extinguishing liquid that is prepared from the fire extinguishing composition of the present invention, reignition will not occur even when flame is applied 5 min after extinguishing of the fire. The composition was also judged to have superior performance in regard to its capacity for preventing reignition, which is a condition for use in localized-discharge fire extinguishing.

## Working Example 2

1.5 parts of casein sodium was slowly added under stirring to 38.5 parts (weight standard, likewise below) of 75% sugar solution in order to uniformly dissolve the casein sodium in the sugar solution. 60 parts of a uniform mixture of 30 parts of halon 2402 (dibromotetrafluoroethane) and 30 parts of carbon tetrachloride was then slowly added dropwise in order to produce a fire extinguishing composition in the form of a uniform mixture.

When the fire extinguishing composition was mixed with water, it readily emulsified and dispersed in the water to produce a uniform fire extinguishing solution, and so various fire extinguishing liquids were prepared as indicated in Table 3. The same fire extinguishing test method as in Working Example 1 was used, and the results presented in Table 3 were obtained.

Table 3

Halon concentration in fire extinguishing liquid (%)	Fire extinguishing time (sec)	Amount of fire extinguishing liquid (cc)	Used amount of halon (cc)
8	Not extinguished	250	20
10	Not extinguished	250	25
12	10	220	26.4
15	8	220	33
20	5	200	40
Water	Not extinguished	250	0
Halon stock solution	7	50	50